

ANALYSIS OF BAUXITE AND OF REFRACTORIES OF HIGH ALUMINA CONTENT

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ABSTRACT

A study has been made of the analytical details involved in the analysis of bauxite and burnt refractories of high alumina content. The work has shown that an accurate analysis of these materials is a far more difficult problem than it is ordinarily thought to be. In spite of the fact that the determination of alumina is usually regarded as very simple, extreme values of 54.84 and 56.68 per cent were reported by the analysts who cooperated on the analysis of the Bureau of Standards standard sample of bauxite No. 69 (actual Al_2O_3 , 55.06 per cent). The results for alumina and silica reported in the analysis of the standard burnt refractories Nos. 76, 77, and 78 were even less satisfactory. The improper drying of bauxite and the difficulty of putting burnt refractories into complete solution were found to be sources of error.

Other sources of error, such as improper ignition of precipitates of aluminum hydroxide, misleading corrections for impurities derived from reagents, etc., are pointed out. An umpire method is given for the determination of SiO_2 , Al_2O_3 , P_2O_5 , Cr_2O_3 , V_2O_5 , Fe_2O_3 , TiO_2 , ZrO_2 , CaO , and MgO . In addition, a routine method for Al_2O_3 is described. In this method the solution of the sample is divided into three aliquots. In the first aliquot the Al_2O_3 , Fe_2O_3 , TiO_2 , ZrO_2 , P_2O_5 , and V_2O_5 are precipitated by NH_4OH . In the second aliquot the Fe_2O_3 , TiO_2 , ZrO_2 , and V_2O_5 are precipitated by cupferron. In the third aliquot the P_2O_5 is determined. The Al_2O_3 is then found by difference.

CONTENTS

	Page
I. General considerations.....	92
II. Methods of analysis.....	93
1. Precautions.....	93
(a) Drying.....	93
(b) Solution of the sample.....	93
(c) Silica.....	94
(d) Alumina.....	95
2. Umpire method for the analysis of bauxite or refractories of high alumina content.....	96
(a) Drying.....	96
(b) Solution of the sample.....	97
(c) Determination of silica.....	97
(d) Determination of the mixed oxides.....	98
(e) Recovery of silica.....	98
(f) Determination of P_2O_5 , Cr_2O_3 , and V_2O_5	99

II. Methods of analysis—Continued.

2. Umpire method for the analysis of bauxite or refractories of high alumina content—Continued	Page
(g) Determination of Fe_2O_3 , TiO_2 , and ZrO_2 (HfO_2)	100
(h) Determination of lime and magnesia	101
(i) Determination of the alkalies	102
3. Routine method for the determination of alumina in bauxite or refractories of high alumina content	102
(a) Precipitation by ammonium hydroxide	103
(b) Precipitation of Fe_2O_3 , TiO_2 , etc., by cupferron	103
(c) Determination of P_2O_5	103

I. GENERAL CONSIDERATIONS

An accurate analysis of bauxite or of refractories of high alumina content is a far more difficult problem than is ordinarily thought. For example, in the A. S. T. M. Standards (1924), page 749, it is stated that—

It shall be considered satisfactory if the differences between check determinations (in refractories) do not exceed the following limits: For silica or other constituents amounting to 30 per cent or over, 0.3 per cent; for alumina or other constituents amounting to 10 to 30 per cent, 0.2 per cent; and for any other constituent amounting to under 10 per cent, 0.1 per cent.

In contrast to these expectations the data given in Table 1 show the extreme values and the average deviation from the standard values for the first analyses reported on Bureau of Standards standard samples of burnt refractories Nos. 76, 77, and 78. Furthermore, in determinations of the percentage of Al_2O_3 in the bureau sample of bauxite No. 69 (55.06 per cent Al_2O_3) the extreme values reported were 54.84 and 56.68, and the average deviation from the standard value was 0.59 per cent.

TABLE 1.—Results reported in first analyses of Bureau of Standards analyzed refractories

Constituent	Sample No. 76			Sample No. 77			Sample No. 78		
	Recommended value	Extreme values	Average deviation	Recommended value	Extreme values	Average deviation	Recommended value	Extreme values	Average deviation
SiO_2	54.68	53.02–55.00	0.43	32.38	30.20–32.76	0.58	20.69	18.26–21.64	0.51
Al_2O_3	37.67	37.47–40.81	.76	59.39	58.82–61.67	1.33	69.97	69.23–74.36	1.68
Fe_2O_3	2.38	.85–3.69	.37	.90	.75–3.46	.46	.79	.63–3.38	.43
TiO_2	2.21	.10–2.70	.35	2.93	.14–3.10	.35	3.37	.17–3.60	.59
CaO	.27	.11–.95	.21	.26	.19–.48	.10	.38	.28–.65	.09
MgO	.58	.08–.71	.23	.50	.09–.58	.18	.51	.03–.70	.19
K_2O	1.37	.87–1.43	.26	2.11	1.16–2.10	.63	2.83	1.84–2.90	.66
Na_2O	.38	.09–1.66	.53	.86	.43–2.17	.59	.53	.32–1.72	.47

It is significant that the differences between the determinations for SiO_2 and for Al_2O_3 were from 7 to 17 times greater than the specified tolerances, and that out of 28 analyses of the refractories 17 results for SiO_2 were lower and 11 were higher than the actual content, while for Al_2O_3 , 6 results were lower and 22 were higher.

It is apparent that there is room for considerable improvement in the analysis of such materials, in spite of the attention that has been paid to methods for determining SiO_2 , Al_2O_3 , and the like. This paper accordingly sets forth suggested umpire procedures, together with such precautions as have been found necessary. In addition, a routine method is suggested for the determination of Al_2O_3 , particularly in bauxite, which provides a simple direct determination of P_2O_5 and obviates the necessity of separate determinations of and deduction for such constituents as Fe_2O_3 , TiO_2 , ZrO_2 , and V_2O_5 , all of which may be present and must be guarded against.

II. METHODS OF ANALYSIS

1. PRECAUTIONS

(a) DRYING.—The moisture content of powdered bauxite varies with atmospheric conditions. In tests made at the Bureau of Standards it was found necessary to dry samples for two hours at 140°C . in order to obtain reproducible results. Material thus dried is so hygroscopic that each portion of sample taken for analysis must be separately dried. Burnt refractories present very little difficulty in drying. Reproducible samples can be obtained by drying for one hour at 105 to 110°C ., and the dried samples are not appreciably hygroscopic.

(b) SOLUTION OF THE SAMPLE.—Bauxite can be almost entirely decomposed by a mixture of HF , HNO_3 , and H_2SO_4 . Such an attack is more convenient than a fusion procedure because the introduction of foreign salts is avoided and SiO_2 is eliminated. HF must afterwards be entirely expelled by fuming with H_2SO_4 , or the subsequent precipitation of aluminum by NH_4OH will be incomplete, and any insoluble residue must be recovered, fused, and put into solution.

Burnt refractories do not respond as well to a wet attack. For these, as well as for bauxite, when SiO_2 is to be determined, recourse must be had to a fusion method. Na_2CO_3 , Na_2O_2 , $\text{K}_2\text{S}_2\text{O}_7$, or $\text{Na}_2\text{S}_2\text{O}_7$ are satisfactory fluxes. At the Bureau of Standards 7 to 10 g of Na_2CO_3 was used for the fusion of a 1 g sample, and the full temperature of a Méker burner was maintained for at least one hour. Of the cooperating analysts, W. F. Muehlberg, of the Newburgh Steel Works, obtained satisfactory results in the analysis of bauxite by exploding the sample in a mixture of Na_2O_2 and sugar carbon,¹ while L. P. Chase,² of the Illinois Steel Co., fused the burnt refractories with $\text{K}_2\text{S}_2\text{O}_7$. According to M. O. Lamar,² of the Norton Co.,

¹ W. F. Muehlberg, *Ind. Eng. Chem.*, **17**, p. 690; 1925.

² Private communication.

satisfactory fusions of calcined bauxite are obtained through the use of equal parts of Na_2CO_3 and fused $\text{Na}_2\text{B}_4\text{O}_7$.³

The melt can be dissolved in dilute HCl or H_2SO_4 , depending upon which reagent is preferred for the dehydration of SiO_2 . If there is any evidence of incomplete decomposition of the sample after either wet or fusion attack, much trouble can be avoided by filtering off the insoluble matter, igniting, fusing with $\text{K}_2\text{S}_2\text{O}_7$ or $\text{Na}_2\text{S}_2\text{O}_7$, and dissolving the melt in the original solution before proceeding with the analysis.

(c) **SILICA.**—Two dehydrations with HCl or H_2SO_4 are sufficient in routine work. If HCl is used, the temperature of dehydration should not exceed 105 to 110° C. on account of the formation of insoluble aluminum compounds. If H_2SO_4 is used, a liberal excess must be present to keep the dehydrated mass from forming a solid cake which renders subsequent solution of the salts most difficult.

The first SiO_2 recovered must be very thoroughly washed with hot dilute HCl (5:95)⁴ and then with hot water to remove salts of aluminum and the alkalis. The smaller second recovery is washed with cool dilute HCl (1:99) and then with hot water. The temperature at which SiO_2 is finally heated must not be less than 1,200° C., and the heating must be continued until constant weight is obtained. As the ignited oxide is somewhat hygroscopic, the crucible should be covered with a well-fitting cover during cooling and weighing, and the desiccator should contain a strong desiccant.

In analyses of the highest accuracy the SiO_2 that escapes two dehydrations must be recovered in the second filtrate by precipitating with NH_4OH , dissolving the precipitate in dilute H_2SO_4 , evaporating to fumes of H_2SO_4 , diluting and filtering. Less accurate, because of the solvent action of KHSO_4 or NaHSO_4 , but satisfactory for most purposes, is the recovery based on the fusion of the weighed oxides as under the umpire method. The amount that is recovered varies. In analyses of a series of refractories with SiO_2 content ranging from 20 to 60 per cent the recoveries averaged 0.2 per cent in either HCl or H_2SO_4 dehydration. It is not safe, however, to arbitrarily add this amount of SiO_2 , because in some cases as little

³ If $\text{Na}_2\text{B}_4\text{O}_7$ is used, it must be removed before determinations of SiO_2 or Al_2O_3 are attempted, for otherwise part of the boron is carried down by SiO_2 and volatilized as the fluoride, BF_3 , while part is carried down by the NH_4OH precipitate in spite of reprecipitations. Boron can be removed as follows: Place the melt in a large porcelain or platinum dish, cover and treat with a saturated solution of HCl in CH_3OH (prepared by passing dry HCl gas into cooled CH_3OH for one to two hours). When effervescence ceases, remove the cover and heat just short of boiling, preferably on a water bath in a good hood. Cleanse the crucible in a similar manner and add its contents to the dish. Add more reagent as necessary until solution is complete, boil to a small volume and evaporate to dryness on the bath. To remove the last traces of boron, evaporate to dryness at 80 to 85° C. on the bath two or three times with successive additions of small portions of the reagent, taking care to wash down the sides of the dish.

⁴ Prepared by mixing 5 ml of HCl sp. gr. 1.19, with 95 ml of water. This system of designating dilute acids is used throughout the paper. For example, dilute H_2SO_4 (1:1), denotes a solution containing 50 ml of H_2SO_4 , sp. gr. 1.84, and 50 ml of water.

as 0.04 per cent was recovered while in others the recovery amounted to 0.3 per cent.

(d) ALUMINA.—The chief sources of error in a determination of Al_2O_3 in bauxite or refractories high in Al_2O_3 are:

1. Failure to completely decompose the material. Whenever there is doubt as to the completeness of decomposition, the residue left after dissolving the melt should be fused, dissolved, and added to the original solution.

2. Failure to fuse the nonvolatile residue left after the treatment of the SiO_2 with HF and H_2SO_4 . This residue must be fused, the melt dissolved, and the solution added to the filtrate from the SiO_2 .

3. Failure to correct for all of the compounds that are normally carried down in the NH_4OH precipitate and weighed with the Al_2O_3 . The following list of such compounds that are contained in the Bureau of Standards sample of bauxite No. 69 illustrates the extent of the errors that may be made if any or all of such corrections are omitted: Fe_2O_3 , 5.66 per cent; TiO_2 , 3.07 per cent; ZrO_2 , 0.08 per cent; P_2O_5 , 0.11 per cent; V_2O_5 , 0.03 per cent; and Cr_2O_3 , 0.04 per cent.

4. Failure to remove the alkali salts carried down by the NH_4OH precipitate. For example, after fusion of 0.5 g of bauxite with 7 to 10 g of Na_2CO_3 and elimination of SiO_2 , the alkali salts in the ignited mixed oxides as determined by the J. Lawrence Smith method amounted to 0.7 mg after careful double precipitation and 0.1 mg after triple precipitation by NH_4OH . The error caused by the retention of alkalis may, therefore, be as high as 0.14 per cent of Al_2O_3 (on a 0.5 g sample) in spite of double precipitations and will be much greater if only a single precipitation is made.

5. Improper ignition of the NH_4OH precipitate. Blum⁵ has shown that Al_2O_3 which has been heated over the blast lamp to constant weight undergoes no further loss upon heating to 1,440 to 1,460° C. As a result of his tests he states that ignition for 5 to 10 minutes over a blast lamp is sufficient to bring Al_2O_3 to constant weight. This statement is correct for small precipitates obtained from pure solutions. In ignitions of the large mixed precipitate obtained from bauxite or refractories the analyst must be sure that he is igniting at at least 1,200° C. and that constant weight has been obtained. For example, a precipitate containing 0.35 g of Al_2O_3 lost but 0.1 mg when heated in a muffle for one hour at 900° C. after a preliminary heating for a like period at 800° C. When heated for one hour at 1,050° C., it lost 1.4 mg, and upon heating over the blast it lost 1.5 mg more, both corrected for the loss of weight of the platinum crucible. The error caused by the retention

⁵ B. S. Sci. Paper No. 286; J. Am. Chem. Soc., 38, p. 1282; 1916.

of water would therefore, have been 0.58 per cent of Al_2O_3 (on a 0.5 g sample) if heating had been stopped at 900°C . and 0.30 per cent if it had been stopped at $1,050^\circ\text{C}$.

6. Failure to protect the ignited residue from moisture before or during weighing. Ignited Al_2O_3 absorbs water readily and takes up in the first few minutes a large proportion of the water that it will absorb in 24 hours. This is important, as the atmosphere in a desiccator immediately after opening is not much different from that of the room. Fortunately, the rate of absorption is very slow if the crucible is covered with a well-fitting lid during cooling and weighing, and errors are negligible if a good desiccant is used in the desiccator and weighings are made rapidly. For example, a well-covered crucible containing 0.1 g of ignited Al_2O_3 showed no appreciable change in weight in five minutes on the balance pan but gained 1 mg in five minutes when uncovered. An oxide ignited at $1,200^\circ\text{C}$. is less hygroscopic than one ignited at $1,000^\circ\text{C}$.

7. Failure to correct for SiO_2 carried down by the NH_4OH precipitate. SiO_2 is always carried down by the NH_4OH precipitate, and the amount depends on the completeness of the recovery of SiO_2 at the start of the analysis and the amount afterwards introduced with the reagents, chiefly through NH_4OH . SiO_2 is always left in solution, even after double dehydration with HCl or H_2SO_4 . In careful analyses the amount (on a 0.5 g sample) may represent as little as 0.05 per cent of Al_2O_3 and as much as 0.3 per cent.

8. Misleading corrections for impurities derived from the reagents or through attack on the vessels used. The small precipitate obtained by precipitation with NH_4OH in a solution of reagents alone does not, as a rule, carry down impurities, such as SiO_2 or P_2O_5 , introduced through the reagents or during the analysis, as completely as does the much larger precipitate obtained from the material under analysis. For example, in analyses of 0.5 g portions of bauxite, an average correction of 0.25 mg was indicated by the reagents alone, 1.8 mg when 0.25 g of Al_2O_3 as pure AlCl_3 was added to the reagents and no correction for SiO_2 was made, and 0.9 mg when AlCl_3 was added and correction for SiO_2 was made. If the correction was based on reagents alone, the result for Al_2O_3 in the bauxite would, therefore, be high and differ by 0.13 from the true percentage. On the other hand, if no correction was made for the SiO_2 carried down by the added Al_2O_3 the result would be low and differ by 0.18 per cent from the true value.

2. UMPIRE METHOD FOR THE ANALYSIS OF BAUXITE OR REFRACTORIES OF HIGH ALUMINA CONTENT

(a) DRYING.—Transfer a portion of the sample to a weighing bottle of such diameter that the layer of sample is not more than one-half

centimeter deep. Dry bauxite for two hours at 140°C . and burnt refractories for one hour at 105 to 110°C . Cool over a good desiccant. In the most accurate analyses of bauxite each portion taken for analysis should be separately dried and the weight obtained by stoppering the bottle, cooling in a desiccator, lifting the cover for an instant, weighing, pouring out as much of the powder as possible without brushing, and again weighing.

(b) SOLUTION OF THE SAMPLE.—Thoroughly mix 0.5000 g of the dried sample with 7 to 8 g of Na_2CO_3 in a platinum crucible and cover the mixture with an additional gram of Na_2CO_3 . Gradually, particularly with bauxite, heat the covered crucible and its contents until the mass is molten. After the mass is molten and the fusion is quiet grasp the crucible with a pair of tongs, slightly tilt and rotate it, so as to decompose particles which cling to the sides of the crucible above the molten mass. Finally heat at $1,000$ to $1,100^{\circ}\text{C}$. for one hour. Cool and dissolve the melt in a platinum dish in 150 ml of dilute H_2SO_4 ($1:9$). If there is any indication of incomplete decomposition, filter the solution, wash the residue, and ignite the paper in the crucible used for the fusion. Fuse the residue with a small amount of Na_2CO_3 and add the cooled melt to the original solution.

If SiO_2 is not to be determined, bauxite can be almost entirely decomposed by the use of HF , HNO_3 , and H_2SO_4 as described in the routine method. Burnt refractories are only partially decomposed by such treatment.

(c) DETERMINATION OF SILICA.—Evaporate the solution until fumes of H_2SO_4 appear, cool, and take up in 200 ml of water. Heat until the salts are in solution, and immediately filter through a No. 40 Whatman or similar paper. Wash very thoroughly with warm dilute HCl ($5:95$) and finally with hot water. It is very important that the SiO_2 be washed free from sodium salts. Reserve the paper and residue. Again evaporate the filtrate until fumes of H_2SO_4 appear and treat as before except that the residue should be washed with cool dilute HCl ($1:99$) instead of with the hot $5:95$ acid. Reserve the filtrate (A). Char the two papers containing the SiO_2 in a platinum crucible, burn the carbon at as low a temperature as possible, and finally heat at approximately $1,200^{\circ}\text{C}$. Cool over a good desiccant and weigh. The heating should be very gentle at first to avoid mechanical loss of very finely powdered SiO_2 , and the crucible must be tightly covered during the final heating. If a blast lamp is used, the crucible should be set to two-thirds of its depth in an asbestos shield.

After constant weight has been attained carefully moisten the SiO_2 in the crucible and add a few drops of H_2SO_4 ($1:1$) and approximately 10 ml of HF . Evaporate, carefully expel the H_2SO_4 , and again ignite to constant weight. The difference between the two

weights is SiO_2 . To this must be added the SiO_2 recovered from the mixed oxides.

(d) DETERMINATION OF THE MIXED OXIDES.—Fuse the nonvolatile residue from the SiO_2 with a small quantity of $\text{K}_2\text{S}_2\text{O}_7$, cool, take up the melt in dilute H_2SO_4 (1:9), and add the solution to the filtrate from the determination of SiO_2 (A). Dilute this solution to 350 ml, add a few drops of methyl red indicator, heat to boiling and add NH_4OH until the red color just changes to a light yellow. Boil for one to three minutes and, if the red color of the indicator reappears, discharge it by adding another drop of NH_4OH . Filter through a No. 40 Whatman or similar paper and wash the precipitate 5 to 10 times with a hot neutral 2 per cent solution of NH_4Cl . Return the precipitate to the beaker in which the precipitation was made by washing it off the paper with a strong jet of water and dissolve it in 50 ml of hot dilute HCl (1:1). When the precipitate has dissolved, dilute to 350 to 400 ml, add the paper, stir until pulped, and repeat the precipitation and washing as before. Do not allow the precipitate to run dry on the filter, but keep the paper filled or nearly filled with wash solution. At least 250 ml of solution should be used in the final washing. If the precipitate is too large to go into the crucible, dry the paper and contents at 100 to 110° C. and then transfer to a platinum crucible that has been weighed with cover. Ignite at a low temperature and under good oxidizing conditions at first and finally cover and heat at approximately 1,200° C. Cool over a good desiccant, never CaCl_2 , and weigh quickly. Repeat the heating and weighing until constant weight is obtained. The precipitate contains the Al_2O_3 , Fe_2O_3 , TiO_2 , ZrO_2 , P_2O_5 , V_2O_5 , Cr_2O_3 ⁶ which were present in the sample, besides the SiO_2 which escaped the double dehydration.

In order to arrive at the true weight of Al_2O_3 , it is necessary to determine the weights of the other substances as described below and to subtract from the total weight. As the quantities of the accompanying substances are relatively small, this method of obtaining Al_2O_3 (by difference) yields results that are quite acceptable, although an accuracy better than 1 part in 200 can hardly be expected.

(e) RECOVERY OF SILICA.—Fuse the mixed oxides with $\text{K}_2\text{S}_2\text{O}_7$, cool, and dissolve the melt in 100 ml of dilute H_2SO_4 (1:9). Evaporate to incipient fumes of H_2SO_4 , cool, add 150 to 200 ml of warm water, heat until the salts are in solution, and immediately filter and wash the small amount of SiO_2 . Reserve the filtrate (B). Ignite, weigh, treat with HF and H_2SO_4 as previously described, and again weigh. Add this SiO_2 to that previously obtained. Fuse the small

⁶ Cr_2O_3 by itself is partially oxidized during ignition and is no doubt partly oxidized during the ignition of the mixed oxides. If the total amount involved is small, as in the usual case, no appreciable error is caused if calculations are based on the oxide, Cr_2O_3 . If large amounts of chromium are present, as in chrome brick, accurate results can only be obtained by determining the chromium (preferably by volumetric titration) in a separate portion of sample and oxidizing it to the chromate before the mixed oxides are precipitated.

nonvolatile residue with a little $K_2S_2O_7$, dissolve the melt in dilute H_2SO_4 , and add to the reserved filtrate (B).

(f) DETERMINATION OF P_2O_5 , Cr_2O_3 , AND V_2O_5 .—Nearly neutralize the combined filtrates (B) with $NaOH$ and pour the solution (not over 100 ml in volume) slowly and with constant stirring into 150 ml of a 10 per cent solution of $NaOH$ containing 1.0 g of Na_2O_2 . Digest on the steam bath for 1 hour to oxidize the chromium to chromate and to decompose the excess of peroxide, cool, and filter through a paper which has been treated with $NaOH$ of the same strength. This treatment of the paper will prevent the extraction of coloring matter from the paper. Wash the precipitate with hot water and reserve it for the determination of Fe_2O_3 , TiO_2 , and ZrO_2 (C). Determine the chromium in the filtrate colorimetrically by comparing the color with that obtained by adding a standard solution of chromate to an alkaline solution of the same strength.

After the color comparison acidify the solution and add a very slight excess of NH_4OH in order to precipitate the aluminum which will also carry down any phosphorus and vanadium present. Do not use an indicator such as methyl red in this precipitation, as its color may subsequently interfere with the determination of vanadium. Litmus is sufficiently sensitive, as phosphorus and vanadium will not be lost unless a large excess of NH_4OH is added. The precipitation with NH_4OH at this point is introduced to get rid of the Na_2SO_4 which would otherwise interfere with the precipitation of phosphorus. Incidentally, the most of any chromium and of elements such as platinum and molybdenum are also removed. Filter, dissolve the precipitate in 100 ml of dilute HNO_3 (1:9), and add a few drops of H_2O_2 . If any color develops, compare with a standard solution of vanadium under the same conditions.

After the vanadium has thus been determined colorimetrically, transfer the solution to a 300 ml Erlenmeyer flask and destroy the H_2O_2 by boiling vigorously for one or two minutes and then adding a saturated solution of $KMnO_4$ dropwise until a pink color persists. Decolorize by the addition of a few drops of H_2SO_3 , add 15 ml of HNO_3 (sp. gr. 1.42), cool, adjust the volume to about 125 ml, and add 40 ml of dilute NH_4OH (sp. gr. 0.96) and 40 ml of molybdate reagent.⁷ Shake for 10 minutes, allow to stand for one-half hour, filter and wash the flask, paper, and precipitate 10 times with a 1 per cent solution of KNO_3 . Return the precipitate and paper to the precipitating flask, add an excess of standard 0.1 N $NaOH$ and 25 ml of water (both free from CO_2), and shake until the precipitate is dissolved. Dilute to 100 ml, add three drops of a 0.2 per cent

⁷ For the preparation of this reagent mix 100 g of pure MoO_3 or 118 g of 85 per cent molybdic acid with 400 ml of water and add 80 ml of NH_4OH (sp. gr. 0.90). When solution is complete, filter and pour the solution slowly and with constant stirring into a mixture of 400 ml of HNO_3 (sp. gr. 1.42) and 600 ml of water. Let settle for 24 hours and use the clear supernatant liquid.

solution of phenolphthalein, and discharge the pink color with standard acid. Finish the titration by adding standard alkali until the pink color reappears. The alkali solution is preferably standardized against the Bureau of Standards acid potassium phthalate or benzoic acid, and the ratio of P_2O_5 to NaOH should be considered as 1:46 in calculating results.

If it is preferred, the phosphorus may be determined gravimetrically by solution of the phosphomolybdate and double precipitation by magnesia mixture.⁸

As the reagents may contain phosphorus, a careful blank carried through all steps of the determination is essential. It is desirable that a known amount of aluminum corresponding to that in the regular analysis be added to the blank. If aluminum is not added, the most if not all of the phosphorus in the reagents would be lost in the precipitation with NH_4OH , while in the regular determination it would be carried down by the aluminum present in the sample. The results for phosphorus would then be correspondingly high.

(g) DETERMINATION OF Fe_2O_3 , TiO_2 , AND $ZrO_2(HfO_2)$.—Dissolve the reserved precipitate (C) in 25 ml of hot dilute HCl (1:2), add 4 g of tartaric acid, dilute with water to a volume of 200 ml, and neutralize with NH_4OH . Add 2 ml of HCl per 100 ml of solution, heat to boiling, and saturate with H_2S . Allow to cool and filter off any platinum sulphide which may have separated and wash with a 1 per cent solution of H_2SO_4 saturated with H_2S . Render the filtrate slightly ammoniacal, pass in a rapid stream of H_2S for five minutes, and digest at the side of the steam bath ($40^\circ C.$) 15 to 30 minutes. Filter and wash with a dilute solution of $(NH_4)_2S$ (5:95) containing 5 g of NH_4Cl per liter. Reserve the filtrate (D).

Dissolve the iron sulphide in hot dilute HCl (1:1) to which has been added a little $KClO_3$, evaporate to dryness, take up in 25 ml of dilute HCl (5:95), and add $KMnO_4$ until the usual pink color is obtained. Reduce with $SnCl_2$ and titrate slowly with a standard solution of $KMnO_4$, as in the Zimmermann-Reinhardt method.

The filtrate (D) contains the titanium and zirconium. Acidify this solution with H_2SO_4 , dilute to 200 ml, adjust the acidity so that the solution contains 10 ml of H_2SO_4 , sp. gr. 1.84 per 100 ml, and cool in ice water. It is unnecessary to destroy tartaric acid. Precipitate the titanium and zirconium with an excess of a cold 6 per cent water solution of cupferron.⁹ An excess of the precipitant is indicated by the formation of a fine white precipitate which redissolves, instead of a curdy one which persists. Stir in a little macerated paper, allow to settle for five minutes, filter by suction through

⁸ G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, **15**, pp. 44 and 171; 1923.

⁹ O. Baudisch, *Chem. Ztg.*, **33**, p. 1298; 1909; W. M. Thornton, jr., *Am. J. Sci.* (4), **37**, pp. 173, 407; 1914; W. M. Thornton, jr., and E. M. Hayden, jr., *Ibid.* (4), **38**, p. 137; 1914; G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **42**, p. 1439; 1920.

a paper and cone, and test the filtrate for complete precipitation. Thoroughly wash the precipitate with cold dilute HCl (1:9). Transfer to a weighed platinum crucible, carefully dry, then cautiously char and burn the carbon, and finally heat at approximately 1,200° C. over a blast lamp or its equivalent. Cool in a desiccator, weigh as $\text{ZrO}_2 + \text{TiO}_2$, and repeat the ignition until constant weight is obtained. The correction of the weighed oxides for SiO_2 by direct treatment with H_2SO_4 and HF is a difficult procedure and is well-nigh impossible if the residue is large. The amount of SiO_2 is usually small and can be determined if desired by evaporating the H_2SO_4 solution of the pyrosulphate melt obtained in the next step to fumes of H_2SO_4 , diluting so that the solution contains 10 per cent of the acid by volume, and recovering the SiO_2 by filtering and washing.

Fuse the precipitate of TiO_2 and ZrO_2 with a small amount of $\text{K}_2\text{S}_2\text{O}_7$, dissolve the melt in 50 ml of dilute H_2SO_4 (1:9), add sufficient H_2O_2 to oxidize all of the titanium (an excess does no harm), add 0.5 g of $(\text{NH}_4)_2\text{HPO}_4$, allow to stand at the side of the steam bath (40° C.) overnight, filter, wash with a 5 per cent solution of NH_4NO_3 , ignite and weigh as ZrP_2O_7 . Calculate to ZrO_2 and subtract from the total weight of $\text{TiO}_2 + \text{ZrO}_2$. As a check, titanium can be determined colorimetrically, before the precipitation of zirconium. In very accurate analyses the ZrP_2O_7 should be fused with a little $\text{K}_2\text{S}_2\text{O}_7$, the melt dissolved in 10 per cent H_2SO_4 as before, and the precipitation repeated. More phosphate must be added in the second precipitation, and an excess of H_2O_2 should be present at all times.

(h) DETERMINATION OF LIME AND MAGNESIA.—For the determinations of CaO and MgO a new and larger sample (1–5 g according to the quantity of CaO and MgO expected) should be used. Put the sample into solution by fusing with Na_2CO_3 or treating with HF, HNO_3 , and H_2SO_4 , as directed under "Solution of the sample." If the solution of the sample is accomplished by fusion with Na_2CO_3 , SiO_2 must be eliminated. Nearly neutralize the SiO_2 -free solution with NaOH, dilute to 100 ml, and pour slowly and with constant stirring into 150 ml of a 10 per cent solution of NaOH containing 1.0 g of Na_2CO_3 . If the sample does not contain iron, it is advisable to make sure of complete precipitation of titanium and to aid the agglomeration of calcium and magnesium by adding about 0.01 g of iron as FeCl_3 to the solution of the sample before pouring it into the NaOH- Na_2CO_3 solution. Digest on the steam bath for one-half hour, allow to cool, filter, and wash a few times with a 1 per cent solution of Na_2CO_3 .

Dissolve the precipitate in 25 ml of hot dilute HCl (1:2), and in this solution precipitate the iron, titanium, etc., by addition of a slight excess of NH_4OH , using methyl red as indicator. Filter,

dissolve the precipitate, and repeat the precipitation with NH_4OH . If it seems desirable to determine iron (provided no iron was added) titanium, and zirconium on a large sample, the precipitate obtained here may be dissolved in HCl and the iron, titanium, and zirconium determined as previously described. In the combined filtrates precipitate the calcium as oxalate in slightly ammoniacal solution, filter, and wash with a cold 1 per cent solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Dissolve the precipitate in a small amount of hot dilute HCl and repeat the precipitation of calcium in a volume of 50 ml. Filter, wash as before, ignite, and weigh as CaO .

Combine the filtrates from the calcium determination, acidify with HCl , and precipitate the magnesium by adding 2 g of $(\text{NH}_4)_2\text{HPO}_4$ to the cold acid solution, then NH_4OH slowly and with stirring until the solution is just alkaline and finally 10 ml in excess. Allow the solution to stand for at least 12 hours, filter, dissolve the precipitate in dilute HCl , and repeat the precipitation in a volume of 50 ml. A few crystals of $(\text{NH}_4)_2\text{HPO}_4$ should be added to the acid solution before the second precipitation. Dry the paper and precipitate in a weighed crucible, char without inflaming, burn the carbon at a temperature below 700°C ., and finally heat at $1,000^\circ$ to $1,100^\circ\text{C}$. Cool in a desiccator and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

(i) DETERMINATION OF THE ALKALIES.—Alkalies can be satisfactorily determined by the J. Lawrence Smith method.

3. ROUTINE METHOD FOR THE DETERMINATION OF ALUMINA IN BAUXITE OR REFRACTORIES OF HIGH ALUMINA CONTENT

Transfer 2.000 g of the dried sample to a platinum dish and add 25 ml of water, 15 ml of concentrated H_2SO_4 , 25 ml of concentrated HNO_3 , and about 20 ml of HF . Cover the dish with a platinum cover and digest on the steam bath for 15 to 30 minutes with occasional stirring. Remove the cover, place the dish over a low flame, and evaporate to copious fumes of H_2SO_4 . Cool, thoroughly wash the inside surface of the dish with a jet of water, mix the contents of the dish thoroughly, and again place over the flame. Heat to incipient fumes of H_2SO_4 , cool, add 50 ml of warm water, and heat until the salts are in solution. If the solution is not entirely clear, add a little macerated paper, filter, wash with hot water, and reserve the filtrate (A). Ignite the paper and residue in a platinum crucible and fuse with the minimum quantity of Na_2CO_3 . Cool the melt and dissolve it in an excess of dilute H_2SO_4 .

If the ignited insoluble residue was small (less than 1 to 2 mg), add the solution of the melt directly to the reserved filtrate (A). If the ignited insoluble residue was large, as is usually the case with high

¹ For example, approximately 15 per cent of the sample was undissolved in tests of a refractory containing 32.38 per cent of SiO_2 and 59.39 per cent of Al_2O_3 .

alumina refractories,¹⁰ it may contain some SiO_2 . In this case add HF and evaporate the solution to incipient fumes of H_2SO_4 . Cool, wash down the sides of the dish, and evaporate as before. Cool, add 50 ml of warm water, and add the solution to the reserved filtrate (A).

When the sample is completely dissolved, cool, transfer it to a 500 ml graduated flask, dilute to the mark, mix, and remove with a pipette (1) a 100 ml portion for precipitation by NH_4OH , (2) a 100 ml portion for precipitation by cupferron, and (3) a 200 or 250 ml portion for the determination of P_2O_5 . (If the percentage of P_2O_5 is low, it is advisable to take as large an aliquot as possible.)

(a) PRECIPITATION BY AMMONIUM HYDROXIDE.—Dilute the first aliquot to 350 ml, add a few drops of methyl red indicator, and proceed as in the umpire method, but make only one precipitation by NH_4OH . The weighed precipitate will contain the Al_2O_3 , Fe_2O_3 , TiO_2 , ZrO_2 , P_2O_5 , V_2O_5 , and more or less of the Cr_2O_3 ¹¹ which were present in the sample.

(b) PRECIPITATION OF Fe_2O_3 , TiO_2 , ETC., by CUPFERRON.—Neutralize the second aliquot with NH_4OH , add 40 ml of dilute, H_2SO_4 (1:1), dilute to 200 ml, and cool in ice water. Precipitate with an excess of a cold 6 per cent water solution of cupferron, filter, wash, ignite, and weigh as in the umpire method for TiO_2 and ZrO_2 . The weighed residue contains the Fe_2O_3 , TiO_2 , ZrO_2 , and V_2O_5 which were present in the sample. Subtract this weight from that of the NH_4OH precipitate to obtain the weight of the $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{Cr}_2\text{O}_3$ in a 0.4000 g sample.

(c) DETERMINATION OF P_2O_5 .—Nearly neutralize the third aliquot with NaOH and pour it slowly and with constant stirring into 100 ml of a 10 per cent solution of NaOH. Allow the precipitate to settle, filter, and wash a few times with a 1 per cent solution of NaOH. Acidify the filtrate with HNO_3 , and precipitate the aluminum and phosphorous by the addition of a slight excess of NH_4OH .¹² Filter wash the precipitate a few times with a 2 per cent solution of NH_4NO_3 . By the use of a spatula transfer the bulk of the precipitate from the paper to the beaker in which the precipitation was made, add 100 ml of dilute HNO_3 (sp. gr. 1.135), heat and digest until the precipitate is dissolved. Pour this solution through the paper to remove any remaining precipitate and catch the clear solution in a 300 ml Erlenmeyer flask. Cool the solution to room temperature, add 40 ml of dilute NH_4OH (sp. gr. 0.96) and 40 ml of molybdate reagent, shake

¹¹ The proportion of the original chromium that is caught in the NH_4OH precipitate is a matter of doubt because of possible oxidation during solution of the sample. Moreover, partial oxidation of the oxide Cr_2O_3 may occur during ignition. Fortunately, so little chromium is usually present in the original material that it can be ignored. In the exceptional case it is best to make sure of its complete oxidation to the sexivalent state during solution of the sample.

¹² The precipitation of phosphorus as ammonium phosphomolybdate is slow or incomplete in the presence of titanium or of large quantities of Na_2SO_4 . Titanium is removed by the first and sodium salts by the second treatment.

for 10 minutes, allow to stand for one-half hour, and proceed as described in the umpire method. Calculate the percentage of P_2O_5 in the sample and subtract from the percentage of $Al_2O_3 + P_2O_5 + Cr_2O_3$, found above.

The routine method can be used as an umpire method if the following refinements are added: (1) Repeat the precipitation with NH_4OH and correct the ignited and weighed precipitate for SiO_2 ; (2) carefully ignite the cupferron precipitate at a low temperature, fuse it with $K_2S_2O_7$, and repeat the precipitation with cupferron.

If a more complete analysis is desired, the precipitate obtained by $NaOH$ preliminary to the determination of phosphorous can be analyzed for Fe_2O_3 , TiO_2 , ZrO_2 , etc.

Three analyses of the Bureau of Standards standard sample of bauxite No. 69 by the routine method gave 55.02, 55.22, and 54.76 per cent of Al_2O_3 as against the certificate value of 55.06.¹³ A single run in which the NH_4OH and cupferron precipitations were repeated gave 54.92. Two analyses of the bureau's burnt refractory No. 77 gave 59.40 and 59.60 per cent of Al_2O_3 by the routine method as against the certificate value of 59.39 per cent.¹⁴ Double precipitations by NH_4OH and cupferron gave 59.18 and 59.38 per cent.

¹³ This sample also contains 5.66 per cent of Fe_2O_3 , 3.07 per cent of TiO_2 , 0.08 per cent of ZrO_2 , 0.11 per cent of P_2O_5 , 0.03 per cent of V_2O_5 , and 0.04 per cent of Cr_2O_3 .

¹⁴ This sample also contains 0.90 per cent of Fe_2O_3 , 2.93 per cent of TiO_2 , 0.09 per cent of ZrO_2 , 0.45 per cent of P_2O_5 , and 0.032 per cent of V_2O_5 .

WASHINGTON, October 31, 1927.

Announcement



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